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NOVEL SUBSTITUTED ISOQUINOLINES

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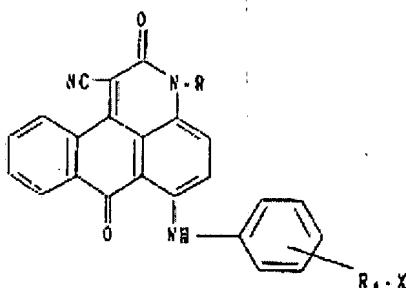
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[Attached amendments do not affect the translation.]

### Claims

1. A compound having the following structure



(in which R is a lower alkyl,

R<sub>1</sub> is a lower alkylene, a C<sub>1-3</sub> lower alkyleneoxy or lower alkylenethio, and

X is one or more substituents selected from the group consisting of hydroxy, carbalkoxy, carboxy and acyloxy).

2. The compound described in Claim 1, wherein R<sub>1</sub> is selected from the group consisting of methylene, ethylene, propylene, butylene, 1,4-tetramethylene, 1,5-pentamethylene, 1,6-hexamethylene, 1,7-heptamethylene, 1,8-octamethylene, methyleneoxy, ethyleneoxy, propyleneoxy, 1,4-tetramethyleneoxy, 1,5-pentamethyleneoxy, 1,6-hexamethyleneoxy, 1,7-heptamethyleneoxy, 1,8-octamethyleneoxy, methylenethio, ethylenethio, propylenethio, 1,4-tetramethylenethio, 1,5-pentamethylenethio, 1,6-hexamethylenethio, 1,7-heptamethylenethio, and 1,8-octamethylenethio.

3. The compound described in Claim 1, wherein

X is selected from the group consisting of carbomethoxy, carboethoxy, carbopropoxy, carbobutoxy, carbamyloxy, carbohexyloxy, carboheptyloxy, carboctyloxy, formyl, acetyl, propionyl, butyryl and valeryl.

4. The compound described in Claim 1, wherein R is methyl and  $R_{1-X}$  is 4-OC<sub>2</sub>H<sub>4</sub>OH.

5. The compound described in Claim 1, wherein R is methyl and  $R_{1-X}$  is 4-C<sub>2</sub>H<sub>4</sub>OH.

6. The compound described in Claim 1, wherein R is methyl and  $R_{1-X}$  is 3-CH<sub>2</sub>OH.

### Detailed explanation of the invention

#### Industrial application field

This patent pertains to novel substituted isoquinolines, their production method and applications as dyes, toners and coloring materials.

#### Prior art

In many cases, a desirable characteristic for a polymer material is its white appearance. For example, fabrics produced from polyester fibers are often expected to have a white appearance in the eyes of an examiner.

Unfortunately, polyester fibers as produced are tinted with a yellowish color that is unacceptable to an examiner.

Currently, toners are incorporated in polyesters to mask the yellowish color and improve the white appearance of the polyester fibers. Said toners in general exhibit a maximum absorption in the range of 575-595 nm when tested in an acetone solution.

#### Problems to be solved by the invention

Cobalt acetate is one of the most widely utilized industrial toners for masking the yellowish color of polymers. However, cobalt acetate has many drawbacks.

For example, cobalt acetate toner materials are unstable at a certain temperature and humidity during storage, and their color tends to shift undesirably to yellow. On the other hand, if a high concentration of cobalt (70 ppm) is required to mask the yellow color of certain polymers, the polymers tend to turn gray.

Secondly, some regulatory organizations are concerned with high concentrations of cobalt.

Thirdly, cobalt reduces the thermal stability of polymers and increases the formation of acetaldehyde in the production of poly(ethylene terephthalate).

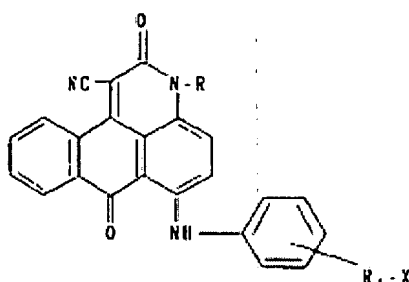
Finally, cobalt forms insoluble residues that accumulate on the inner walls of reactors, creating quality problems in products.

Accordingly, toners or dyes that can improve the appearance of polymers such as polyesters while having no particular drawbacks associated with conventional toners such as cobalt acetate are greatly desired.

Means to solve the problems

We discovered a group of novel isoquinolines that are applicable as toners, dyes or color agents for polymers and other materials while having no drawbacks that many toners, dyes or color agents of the prior art have.

The novel isoquinolines of the present invention are substituted 1-cyano-3H-dibenzo[f, ij]isoquinoline-2,7-dione compounds having the following structural formula



(in which R is a lower alkyl,

R<sub>1</sub> is a lower alkylene, a C<sub>1-3</sub> lower alkyleneoxy or lower alkyleneethio, and

X is one or more substituents selected from the group consisting of hydroxy, carbalkoxy, carboxy and acyloxy).

Preferred R groups include alkyls of 1-8 carbons, and examples include methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl and octyl, and isomers thereof.

Preferred R<sub>1</sub> substituents include methylene, ethylene, propylene, butylene, 1,4-tetramethylene, 1,5-pentamethylene, 1,6-hexamethylene, 1,7-heptamethylene and 1,8-octamethylene.

Preferred lower alkyleneoxy groups include methyleneoxy, ethyleneoxy, propyleneoxy, 1,4-tetramethyleneoxy, 1,5-pentamethyleneoxy, 1,6-hexamethyleneoxy, 1,7-heptamethyleneoxy and 1,8-octamethyleneoxy.

Examples of lower alkyleneethio groups include methyleneethio, ethyleneethio, propyleneethio, 1,4-tetramethylenethio, 1,5-pentamethylenethio, 1,6-hexamethylenethio, 1,7-heptamethylenethio, and 1,8-octamethylenethio.

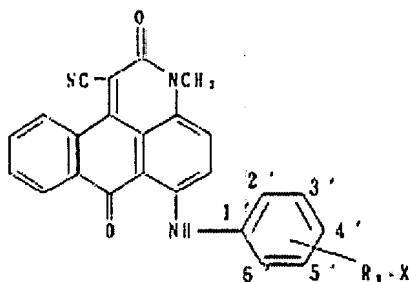
The X groups of the novel compounds are groups capable of forming esters by esterification or by ester exchange reactions.

Preferred X groups include hydroxy, carboxy and carbalkoxy, and examples include carbomethoxy, carboethoxy, carbopropoxy, carbobutoxy, carbamyloxy, carbohexyloxy, carboheptyloxy and carboctyloxy, and isomers thereof.

When X is an acyloxy group, the acyl residual group is derived from aliphatic or aromatic carboxylic acids of 1-20 carbons. Typically preferred acyl residual groups are those derived from formic acid, acetic acid, propionic acid, butyric acid, valeric acid, hexanoic acid, heptanoic acid, octanoic acid, benzoic acid and naphthalic acid, and compounds derived from isomers thereof.

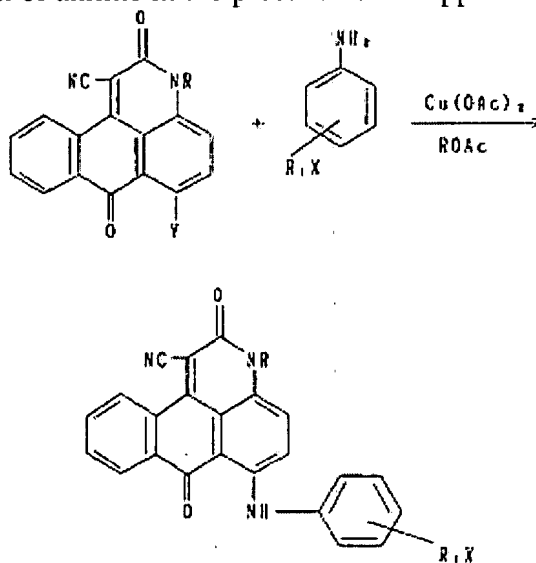
With respect to the definitions for said  $R_1$  and X groups, it should be made clear that these groups may contain one or more substituents such as halogen, alkoxy, cyano and amido groups as long as the validity of the novel compounds is not compromised. Compounds derived in the aforementioned manner are within the embodiment of the present invention and of the applications described herein.

A preferred compound of the present invention is represented by the formula



(in which  $R_{1-X}$  is  $-OC_2H_4OH$ ,  $-C_2H_4OH$  or  $-CH_2OH$ , and preferably arranged at the 4' position or 3' position).

The compound of the present invention can be produced by a modified Ullmann reaction involving nitrogen-arylation of aniline in the presence of a copper catalyst.

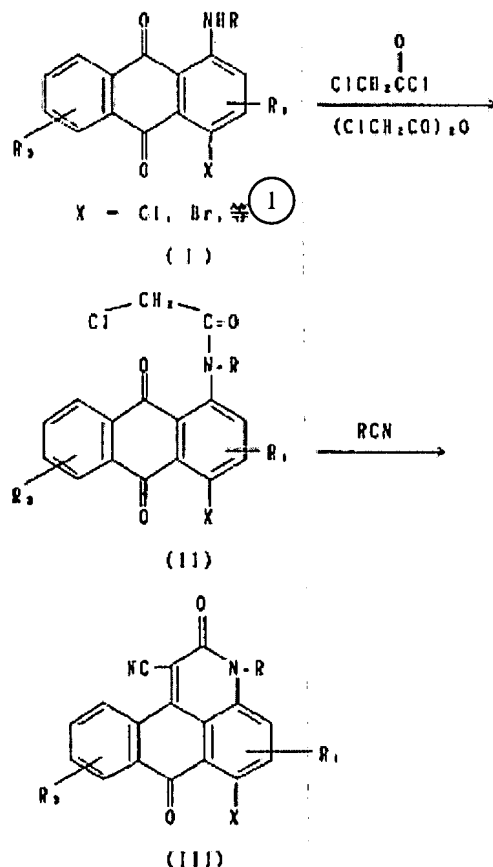


(provided Y is a halogen, and R, R<sub>1</sub> and X are as previously defined)

Typically, the reaction is conducted in the presence of a copper salt in a catalytic quantity together with an appropriate base. Halogenated dibenzoisoquinolinedione reacts with the amino group of aniline to produce an aniline derivative of dibenzoisoquinolinedione, and the product is recovered and purified by conventional methods including removal of solvent, filtration and recrystallization.

Among the aforementioned reactants, aniline is a known and commercially available compound. Halogenated dibenzoisoquinolinedione as a starting material is generally prepared by the following method described by Allen, C. F. H. in *JACS*, pp. 585-588 (1950).

The intermediate 1-amino-4-halogenoanthraquinone (I) is reacted with chloroacetyl chloride or chloroacetyl anhydride to give 1-(chloroacetamide)-4-halogenoanthraquinone (II), which is then treated with an alkali metal cyanide such as potassium cyanide to undergo ring closure and produce halogenated dibenzoisoquinolinedione (III).



Key: 1 etc.

The compounds of the present invention are useful as dyes, toners and coloring agents, either alone or in combination with other compounds.

The compounds of the present invention are particularly useful as toners for synthetic, semisynthetic and natural polymeric materials.

Typical examples of such polymeric materials are bifunctional or polyfunctional compounds having groups that can undergo condensation.

Examples of said polycondensation products include saturated polyesters such as polyesters, poly(ethylene terephthalate) in particular, and polycarbonates produced by polymerizing diols and carboxylates or acid chlorides.

Other polymeric materials for which the aforementioned compounds can be incorporated include cellulose esters of various degrees of esterification and semisynthetic organic materials such as regenerated cellulose.

Natural polymeric materials for which the aforementioned compounds can be incorporated include materials having celluloses, proteins, cotton, wool, linen and silk as the base materials.

The substituted cyano-dibenzoisoquinolinedione compounds can be blended in polyesters during the copolymerization of polycondensation reaction or they can be mixed with polyester polymers. The reactive groups of the toner compounds of the present invention capable of being esterified can serve as groups for terminating chain reaction by adding said compounds during the polycondensation reaction.

Said toner compounds can be incorporated in the polyester structure as terminal groups in the polyester molecules. In this case, the toner molecule is bonded to the polymer molecule by the main atomic force of the ester bonding.

Or, the compounds of the present invention can be utilized by simply adding the compounds in polyesters and mixing therein, followed by mix-melting with a conventional device such as a 2-roller machine, or by blending into polyesters by mixing the compounds with melted polyesters during the fiber spinning process.

The most significant characteristic of the polyesters utilized in the present invention for blending with the compounds described herein is that the physical or chemical properties that are desired for polyester materials are not changed when said compounds are incorporated to become a part of the polymers or are included simply as a mixed substance.

A general problem in the polymerization of polyesters is that physical properties such as the melting point or the tensile strength are adversely affected when a co-monomer or a chain-reaction terminator is included in the polymerization.

By simply exerting its action mechanism on the polymerization reaction, a chain-reaction terminator reduces the molecular weight of the polymer system and lowers the optimum physical and chemical properties of polyesters derived from these compounds.



The cyanodibenzoisoquinolinedione compounds of the present invention exhibit the effect of improving the apparent whiteness of polyesters even when an extremely small quantity is incorporated in the polyesters. For example, even a quantity of less than 10 ppm with respect to the weight of the polyester can give an excellent result.

Accordingly, the compounds of the present invention impart almost no effect on the average molecular weight of polyesters or on the physical and chemical characteristics pertaining to the polyesters when such as a minute quantity is added.

Specifically, the compounds of the present invention have the ability to provide an extremely strong absorption power to polyesters based on their inherent portion in the chemical structures and can impart apparent whiteness to polyester polymers even when an extremely small quantity is utilized.

Other objectives, advantages and characteristics of the present invention are easily comprehensible to those skilled in the art from the following description.

The polyesters and co-polyesters useful in the present invention are obtained by the reaction of at least one glycol of the  $\text{HO}(\text{CH}_2)_n\text{OH}$  type (where  $n$  represents an integer of 2-10) and an alicyclic glycol with at least one dicarboxylic acid or an ester-forming derivative thereof.

Examples of dicarboxylic acids or ester-forming derivatives thereof include terephthalic acid, isophthalic acid, 2,6-naphthalene dicarboxylic acid,  $p,p'$ -dicarboxydiphenyl,  $p,p'$ -dicarboxydiphenylsulfone,  $p,p'$ -dicarboxydiphenylmethane, 1,4-cyclohexanedicarboxylic acid, 1,3-cyclohexanedicarboxylic acid, succinic acid, glutaric acid, adipic acid, 1,12-dodecanoic acid, and aliphatic esters, aryl esters, semi-esters and acid halides thereof.

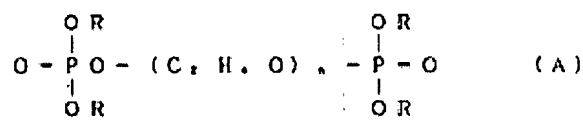
Examples of polyhydric alcohols utilizable in the implementation of the present invention include ethylene glycol, 1,4-cyclohexane dimethanol, 1,2-propanediol, 1,3-propanediol, 1,4-butanediol, 2,2-dimethyl-1,3-propanediol, 1,6-hexanediol, 1,2-cyclohexanediol, 1,4-cyclohexanediol, 1,2-cyclohexanedimethanol, diethylene glycol, and  $x,8$ -bis(hydroxymethyl)tricyclo[5.2.1.0]-decane (where  $x$  represents 3, 4 or 5).

A preferred method for preparing the polyester for blending with the toner of the present invention is described in the following.

Dimethylterephthalate and at least one glycol such as ethylene glycol, a suitable catalyst and less than 10 ppm of a toner of the present invention are fed to a reactor, and the mixture is heated at about 200-225°C for about 140 min in a nitrogen gas atmosphere.

In said first stage of transesterification, bis-glycolate of terephthalate is formed, which is not isolated but is utilized directly in the second stage for producing polyester.

After the transesterification, a catalytic inhibitor consisting of a phosphate ester is added to the reaction product to carry out polycondensation of the reaction product. Preferred phosphate esters have the following formula



(in which n averages 1.5 to about 3.0, and about 1.8 is most preferred;

R is a hydrogen atom or an alkyl group of 6-10 carbons, and an octyl group is the most preferred; the ratio of hydrogen atoms as R to phosphorus atoms is about 0.25-0.50, and about 0.35 is most preferred). The degree of free acid is about 0.2-0.5 for the ester. The quantity of phosphorus is 13-240 ppm versus the acid portion of the ester produced. Other phosphoric esters useful in the present invention include acidic ethyl phosphate, acidic diethyl phosphate, acidic triethyl phosphate, aryl alkyl phosphate and tris-2-ethylhexyl phosphate. Preferred phosphoric esters were disclosed in the detailed description of U.S. Patent No. 3,962,189.

In the second stage, the reaction is carried out at reduced pressure. The pressure is maintained at about 0.2-0.5 mm Hg, and the polycondensation is carried out at about 278°C.

A reduced pressure is required for removing the free polyhydric alcohol, and said alcohol evaporates under these conditions and is removed from the system. The polyesters obtained by said polymerization method are as clear as water and are very desirably tinted with an extremely pale blue color compared to polyesters that exhibit an undesirable yellowish color when prepared without the blue toner.

In addition to the improved white appearance, the polyesters prepared in such manner are thermally stable under the polymerization conditions and are also stable to light or other environmental factors, and furthermore, incorporating such compounds imparts no friction loss to the polymer.

#### Application examples

A general description of the present invention was given above. A better understanding may be attained by referring to certain specific examples of the present invention given below, but these are only examples and are not to be construed as limiting the scope of the present invention unless otherwise specified.

The following application examples describe methods for preparing the compounds of the present invention as well as methods for incorporating these compounds in polymeric materials, particularly for blending with polyesters.

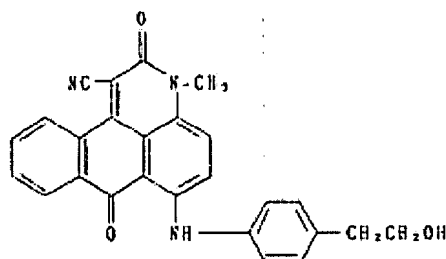
#### Application Example 1 Preparation of 1-cyano-6-[4'-(2-hydroxyethyl)anilino]-3-methyl-3H-dibenzo[f, ij]isoquinoline-2,7-dione

A mixture of 6-bromo-1-cyano-3-methyl-3H-dibenzo[f, ij]isoquinoline-2,7-dione (2.0 g), p-aminophenylethanol (15 g), potassium acetate (2.0 g), cupric acetate (0.2 g) and butanol

(10 mL) was heated slowly to about 80°C and heated continuously for 5-10 min by maintaining the temperature. Afterward, the mixture was added to 10% HCl (250 mL).

The solid product was collected by filtration, and the product was washed with water and air-dried, followed by recrystallizing twice from nitrobenzene to remove red impurities and trace amounts of the starting materials.

The yield of the product obtained was 0.65 g. A solution of the product in acetone exhibits a maximum absorption at 587 nm in the visible region, and the acetone solution shows a blue color tinted with red. The structure of this compound is shown in the following.



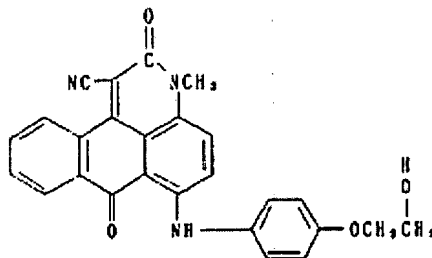
Application Example 2 Preparation of 1-cyano-6-[4'-(2-hydroxyethoxy)anilino]-3-methyl-3H-dibenzo[f, ij]isoquinoline-2,7-dione

A mixture of 6-bromo-1-cyano-3-methyl-3H-dibenzo[f, ij]isoquinoline-2,7-dione (2.0 g), p-aminophenoxyethanol (10.0 g), potassium acetate (2.0 g), cupric acetate (0.5 g) and n-butanol (25 mL) was heated on a steam bath for 1 h while stirring.

The warm reaction mixture was added to acetone (200 mL), and the solid product was collected by filtration and washed with acetone, followed by adding to 10% HCl (150 mL) and mixing at about 60°C while stirring.

The dye was collected by filtration, washed with hot water and then with methanol. Subsequently, the product was air-dried.

Recrystallization from nitrobenzene yielded 0.6 g of an essentially pure, blue toner having the following structure.



Application Example 3 Preparation of poly(ethylterephthalate) copolymerized with 30 mol% 1,4-cyclohexane dimethanol and 4 ppm 1-cyano-6-[4'-(2-hydroxyethoxy)anilino]-3-methyl-3H-dibenzo[f, ij]isoquinoline-2,7-dione blue toner

The following compounds were added to a 500-mL round-bottom flask.

97 g (0.5 mol) dimethyl phthalate,

23 g (0.16 mol) 1,4-cyclohexane dimethanol (70% trans isomer),

52.1 g (0.64 mol) ethylene glycol,

0.22 mL n-butanol solution of acetyl triisopropyl titanate containing 0.0066 g titanium,

1.25 mL ethylene glycol solution of  $\text{Mg}(\text{OCOCH}_3)_2 \cdot 4\text{H}_2\text{O}$  containing 0.006 g manganese [sic; magnesium] and

4 mL acetone solution containing 0.000436 g (4 ppm) 1-cyano-6-[4'-(2-hydroxyethoxy)anilino]-3-methyl-3H-dibenzo[f, ij]isoquinoline-2,7-dione blue toner.

The flask was equipped with a nitrogen gas inlet, a metal stirrer, an exhaust gas outlet and a cooling condenser. The flask and the content were heated on a Belmont metal bath at 200°C for 60 min, followed by heating at 225°C for 80 min to carry out transesterification while passing nitrogen gas over the reactants.

After the ester exchange reaction, the aforementioned phosphate (A) was added to the reaction mixture at a quantity to supply approximately 125 ppm phosphorus with respect to the final theoretical mass of the polymer, and polycondensation of the reaction product was carried out.

The temperature of the metal bath was then increased to 278°C.

Next, a vacuum was drawn on the flask, and the flask and the content were heated at 278°C for 60 min at about 0.2-0.5 mm Hg [sic; mm Hg] pressure to complete the polycondensation.

The flask was removed from the metal bath, followed by cooling in a nitrogen atmosphere. The amorphous polymer produced was as clear as water and was tinted with a very desirable pale blue color (polyester prepared without incorporating the blue toner was yellowish).

The intrinsic viscosity of the produced polymer was 0.77 measured at a concentration of 0.5 g per 100 mL in phenol-tetrachloroethane at a weight ratio of 60/40. Gas chromatographic analysis of a hydrolyzed sample of the product showed that the polyester contained 30 mol% 1,4-cyclohexane dimethanol.

Application Example 4 Preparation of poly(1,4-cyclohexene-dimethylterephthalate) copolymerized with 37 mol% ethylene glycol and 4 ppm 1-cyano-6-[4'-(2-hydroxyethyl)anilino]-3-methyl-3H-dibenzo[f, ij]isoquinoline-2,7-dione blue toner

The following compounds were added to a 500-mL round-bottom flask.

97 g (0.5 mol) dimethyl phthalate,  
49 g (0.34 mol) 1,4-cyclohexane dimethanol (70% trans isomer),  
40.9 g (0.66 mol) ethylene glycol,  
0.25 mL n-butanol solution of acetyl triisopropyl titanate containing 0.0075 g titanium,  
1.42 mL ethylene glycol solution of  $\text{Mg}(\text{OCOCH}_3)_2 \cdot 4\text{H}_2\text{O}$  containing 0.0068 g manganese and

4.5 mL acetone solution containing 0.0004905 g (4 ppm) 1-cyano-6-[4'-(2-hydroxyethyl)anilino]-3-methyl-3H-dibenzo[f, i]isoquinoline-2,7-dione blue toner.

Polymerization was carried out in the same manner as in Application Example 3.

The amorphous polymer produced was as clear as water and was tinted with a very desirable pale blue color (polyester prepared without incorporating the blue toner was yellowish). The intrinsic viscosity of the produced polymer was 0.97. Gas chromatographic analysis of a hydrolyzed sample of the product showed that the polyester contained 37 mol% ethylene glycol.

The present invention was described in detail; however, it is obvious to those skilled in the art that many changes and modifications can be conducted without deviating from the spirit and scope of the present invention.